

# Movement of metolachlor in soil: effect of new organo-clay formulations

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**Abstract:** The use of commercially available formulations of metolachlor has resulted in its leaching and migration to water sources. Formulations of metolachlor designed to reduce its leaching in soil have been prepared by adding the herbicide dissolved in an organic solvent or in water to organo-clay complexes. Best formulations were made when the organo-clay complex was formed by adsorbing the monovalent organic cations benzyltrimethylammonium (BTMA) or benzyltriethylammonium (BTEA) onto sodium montmorillonite (Mont) at 0.5 or 0.8 mole kg<sup>-1</sup> clay. Adsorption of metolachlor to organo-clays followed the sequence Mont-BTMA 0.5 > Mont-BTMA 0.8 > Mont-BTEA 0.8 > Mont-BTEA 0.5 > Mont. Fourier transform infrared (FTIR) analysis demonstrated the occurrence of shifts of several peaks of adsorbed metolachlor relative to the free herbicide, indicating the existence of strong interactions between metolachlor molecules and the organo-clay surface. Leaching studies employing organo-clay and commercial formulations were carried out under greenhouse and field conditions. Metolachlor applied as organo-clay formulations leached less than the commercial formulation. Organo-clay formulations prepared by adding the herbicide as a water solution showed less leaching in the soil profile than those made by using organic solvent. Under greenhouse conditions, the herbicidal activity of organo-clay formulations was similar to that of the commercial one. Under field conditions, leaching from Mont-BTMA 0.5-metolachlor was less than that from the commercial formulation, demonstrating the environmental and agricultural advantages of the organo-clay formulations of metolachlor.

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**Keywords:** montmorillonite; benzyltrimethylammonium; benzyltriethylammonium; leaching, phytotoxicity; herbicidal activity

## 1 INTRODUCTION

Metolachlor is a selective pre-emergence herbicide widely used in irrigated crops such as potato, peanuts, corn and sunflower to control annual weeds including crabgrass (*Digitaria ciliaris* (Retz) Koel), foxtails (*Setaria* spp), pigweed (*Amaranthus hybridus* L), purslane (*Portulaca oleracea* L), and the perennial weed yellow nutsedge (*Cyperus esculentus* L).<sup>1</sup> Contamination of ground and surface water with metolachlor has been detected in some US states and Canadian provinces,<sup>2–4</sup> and in Europe.<sup>5</sup> High levels of metolachlor have also been detected in run-off and sub-surface water.<sup>6</sup> Mobility of metolachlor in the soil profile has been extensively studied.<sup>7–9</sup>

The migration rate of metolachlor in soil columns was increased with increased dose,<sup>10</sup> and with increased rainfall or irrigation rate following herbicide application.<sup>11</sup> The magnitude of herbicide movement in soil depends on spatial and temporal distribution of soil water that is normally different under fallow conditions from that under cropped conditions.<sup>12</sup> Time of dissipation of 50% of metolachlor ranged from 85 to >106 days.<sup>13</sup> Greater persistence was reported at lower temperatures and at greater depth.<sup>14</sup> Increased sorptivity of metolachlor in soil has been positively correlated with clay,<sup>15–17</sup> humic,<sup>18</sup> and organic matter content.<sup>19</sup>

It is well established that the herbicidal activity of

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metolachlor may be lost due to its mobility in the soil profile. Several attempts have been made to prepare formulations of metolachlor that would be environmentally and agriculturally acceptable. These attempts involved the use of starch encapsulation,<sup>20</sup> and tablet forms.<sup>21</sup> Weed control efficacy was similar with both starch-encapsulated and commercial formulations of metolachlor at low weed densities (122 total plants m<sup>-2</sup>), but less efficacy was observed with starch encapsulation than with the commercial formulation at a high weed density (740 plants m<sup>-2</sup>).<sup>22</sup>

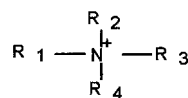
Our approach was to achieve slow release of herbicide molecules by adsorbing them on clay minerals, which are natural components of soils. The adsorption of organic molecules to clays has been extensively studied.<sup>23–30</sup> The organo-clays were prepared by adsorbing to clays substituted quaternary ammonium ions [(CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>R or (CH<sub>3</sub>)<sub>2</sub>N<sup>+</sup>RR'], where R and R' are aromatic or alkyl species. This exchange modifies the clay surface from hydrophilic to hydrophobic.<sup>31,32</sup>

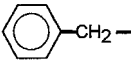
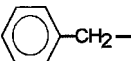
In the present study we prepared new organo-clay based formulations of metolachlor and conducted laboratory and field trials similar to those recently reported for alachlor,<sup>33</sup> whose chemical structure is similar to that of metolachlor. Our main idea has been to adsorb metolachlor to clays whose surfaces were modified from hydrophilic to hydrophobic by the adsorption of a suitable organic cation. Such modified surfaces may enhance the adsorption of non-polar herbicides, thus reducing the concentrations available for leaching in the soil profile and consequently extending their herbicidal activity in the field.<sup>34,35</sup>

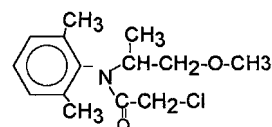
## 2 EXPERIMENTAL METHODS

### 2.1 Chemicals

The clay used was sodium montmorillonite SWy-1 (Mont) obtained from the Source Clays Repository, Clay Minerals Society, Columbia, MO. Its cation exchange capacity (CEC) was 0.8 mole kg<sup>-1</sup> clay.<sup>36</sup> Analytical grade metolachlor, purity 99%, (Chem Service, West Chester, PA, USA) was used for making the organo-clay formulations, and a commercial (Dual, 960 g kg<sup>-1</sup> EC Novartis Crop Protection AG, Switzerland) was used as a standard formulation. HPLC grade ethyl acetate, isooctane, BTMA and BTEA were purchased from Sigma-Aldrich (Sigma Chemical Co, St. Louis, MO, USA; Aldrich Chemical Co, Milwaukee, WI, USA). The chemical structures of the organic cations are shown in Fig 1. Rehovot sandy soil (sand 95.5%; silt 3.3%; clay 1.2%; OM 0.2%; pH 7.5) and Gaza sandy soil (sand 93%; silt 1.0%; clay 6%; OM 0.7%; pH 8.0), were collected from 0 to 30 cm depth at the Faculty of Agriculture Experimental Farm in Rehovot and the Agricultural Experimental Station of EPRI in Gaza Strip, respectively. Green foxtail (*Setaria viridis* (L) Beauv) and/or wheat (*Triticum aestivum* L, cv Ariel) were used as test plants.



Name	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
BTMA		-CH <sub>3</sub>	-CH <sub>3</sub>	-CH <sub>3</sub>
BTEA		-CH <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>3</sub>



Metolachlor

Figure 1. Chemical structures of the molecules used.

### 2.2 Experimental conditions

The organo-clay complexes were prepared by drop-wise addition of aliquots of a 10 mM aqueous solution of BTMA or BTEA to a 10 g litre<sup>-1</sup> aqueous suspension of the clay under continuous stirring.<sup>37</sup> After centrifugation (30 min, 16000 g), the precipitate was washed three times with distilled water, lyophilised, ground to <50 µm and kept at room temperature. The cationic loads were determined by CNHSO analyser (Carlo-Erba 1108, Fisons Co, Milan, Italy.) and by UV-vis absorption (Uvikon 810 spectrophotometer Hewlett-Packard Company, Waldbronn 2, Germany).

### 2.3 Adsorption isotherms of metolachlor

Adsorption isotherms were determined in the range of 0–700 µmol metolachlor g<sup>-1</sup> clay pre-adsorbed with BTMA or BTEA. Appropriate aliquots of an aqueous stock solution of metolachlor (10<sup>-4</sup> M) were diluted in distilled water (25 ml) and added under continuous stirring to 5 ml of 5 g kg<sup>-1</sup> clay-complex suspension in a 40-ml centrifuge tube. The final concentration of the organo-clay complexes was 0.83 g litre<sup>-1</sup>. The samples were kept under continuous horizontal agitation at 25(±1) °C for 24 h. The supernatant was separated by centrifugation at 20000 g for 1 h. Sample extraction was conducted by adding sodium chloride (2.4 g) into a glass tube, combined with 10 ml of supernatant and 10 ml of ethyl acetate + isooctane (1 + 9 by volume). The tubes were sealed and vortexed for 2 min at the highest speed, and stored at room temperature for 1 h until the ethyl acetate/isooctane separated. The ethyl acetate/isooctane layer was collected into 25-ml volumetric flasks. The extraction procedure was repeated twice. The extracts were brought to volume (25 ml) with the same solvent mixture, transferred to crimp vials, sealed and analysed using a Hewlett-

Packard Model 6890 gas chromatograph, equipped with electron-capture detector. A Rtx<sup>R</sup>-5MS capillary column (30 m × 0.25 mm internal diameter, 0.25 µm film; Restek Corporation, Bellefonte, PA, USA) was used with nitrogen as the carrier gas at a flow-rate of 2 ml min<sup>-1</sup>. The nitrogen make-up flow-rate was 30 ml min<sup>-1</sup>. The injector and detector temperatures were 250 and 280 °C, respectively; the column was programmed at 170 °C for 1 min, then the temperature was increased at a rate of 5 °C min<sup>-1</sup> to 250 °C and finally held at this temperature for 5 min. Blank recovery was 102(±3)%.

## 2.4 Fourier transform infrared (FTIR)

FTIR spectroscopy was used to examine the interaction between metolachlor and the clay pre-adsorbed by the respective organic cations as previously described.<sup>38</sup> FTIR spectra were obtained using Potassium bromide pellets with a Nicolet Magna-IR-550. Spectra were recorded at room temperature in the range of 1800–1200 cm<sup>-1</sup>. Difference spectra were obtained by subtracting the spectra of corresponding organo-clay, or homo-ionic clay from the spectra of clay-organic cation-metolachlor complexes, or clay-metolachlor complexes.

## 2.5 Preparation of the formulations

### 2.5.1 Employment of organic solvents

The Mont-metolachlor formulations were prepared by dissolving appropriate amounts of metolachlor in acetone and adding it to the suspended powdered clay, or organo-clay in the same solvent with a total volume of 100 ml. The solvent was evaporated under reduced pressure. Several loads of metolachlor (50, 130, 200 and 300 g kg<sup>-1</sup>) on the clay-complex were prepared and examined.

### 2.5.2 Water method

Technical grade metolachlor (530 mg, the solubility limit) was dissolved in one litre distilled water. One gram of dry organo-clay complex was added to the stock solution under continuous stirring for 24 h. The precipitate (pellet) was separated by centrifugation at 15000 g, air dried or lyophilised, and kept in a plastic bottle in the refrigerator. The equilibrium concentration of metolachlor in the supernatant was determined by gas chromatography (GC). The difference between the initial and equilibrium concentrations gave the amount of metolachlor adsorbed to the organo-clay complex.

## 2.6 Leaching studies in the laboratory

Tin macro-columns, 10 × 10 cm surface area, 25 cm height, and micro-columns made of polyethylene tubes, surface area 5 cm<sup>2</sup>, 25 cm height, were filled with a sandy soil, which had been air-dried and sieved through a 2-mm screen. The macro-column surface was sprayed with various formulations of metolachlor at 2.0 kg AI ha<sup>-1</sup> using an atomizer, which discharged the herbicide in 10 ml water, whereas in the micro-

column the herbicide was applied with a pipette which discharged the herbicide in 1 ml water. The columns were carefully irrigated with 500 m<sup>3</sup> ha<sup>-1</sup> applied in portions (up to 50 ml each) during 3–5 h with 20-min intervals. This irrigation level was selected to ensure that the soil in the whole column length would be moistened. The columns were left for 24 to 48 h for equilibration, and then the tin columns were sliced along their lengths, hence forming two pots 10 × 5 × 25 cm each. Two test plant species, green foxtail and wheat were sown in each part in two rows. To ensure germination and growth, the pots were sprinkle irrigated as needed. The micro-columns were sealed from the top, placed horizontally, and sliced along their lengths. One row of green foxtail, or wheat was sown along the length of the micro-columns. Shoot height and weight determined 16 days after sowing were used as indicators to estimate the herbicide presence at different soil depths in the column. Percentage of shoot growth inhibition at any soil depth was calculated according to the following formula:

$$\% \text{Growth Inhibition} = 100 * (P_c - P_t) / P_c \quad (1)$$

where  $P_c$  is the shoot height of the control and  $P_t$  is that of the treated samples at any soil depth.

## 2.7 Leaching studies in the field

Experiments were conducted at two locations: in Rehovot and in EPRI, Gaza Strip during 1996 and 1997. Beds (1 m wide and 5 m long) were prepared using a rotary tiller. One rate of both the commercial and the organo-clay formulations of metolachlor at 2.0 kg AI ha<sup>-1</sup>, along with the corresponding amount of the organo-clay complex without metolachlor were applied pre-emergence using a back-pack motorized sprayer at spray volume of 300 litre ha<sup>-1</sup> at 245 kPa. A sprinkler irrigation system was used to water the field sites at 500 m<sup>3</sup> ha<sup>-1</sup> in both locations. Two days after irrigation, 15 soil samples were taken using one half of the tin metal column gently inserted into a depth of 25 cm in each plot, supported with a wide spatula to ensure complete removal of the soil in the column. The full column was carefully removed and transferred to a greenhouse. One row each of green foxtail and wheat seeds were sown in each column as described above. Presence of the herbicide formulations was estimated at various soil depths by measuring the shoot height or fresh weight of the test plant. The columns were arranged in a completely randomized design with five replications per treatment. Percentage growth inhibition at any soil depth was calculated according to eqn (1).

## 2.8 Phytotoxicity of the formulations

Green foxtail (10 seeds) was planted in pots filled with 100 g air-dried sandy soil (Rehovot). The pots had four holes at the bottom covered with tissue paper. Metolachlor formulations were applied pre-emergence

at various rates (0.0; 0.25; 0.5; 1.0; 2.0; 3.0; 4.0 and 6.0 kg AI ha<sup>-1</sup>) using a chain-driven laboratory sprayer. The experiments were arranged in a completely random design with five replications. Shoot height and fresh weight were determined two weeks after treatment and percent growth inhibition was calculated using eqn (1).

### 2.9 Data analysis

The growth inhibition data were subjected to analysis of variance, and main effects and interactions were tested for significance using repeated measures ANOVA. Univariate comparisons of mean growth inhibition at different depths were performed by Tukey's test ( $\alpha=0.05$ ). Means of effects of different formulations on herbicidal activity were compared by Tukey's test at  $\alpha=0.05$ , following one-way ANOVA.

## 3 RESULTS

### 3.1 Preparation of organo-clay complexes

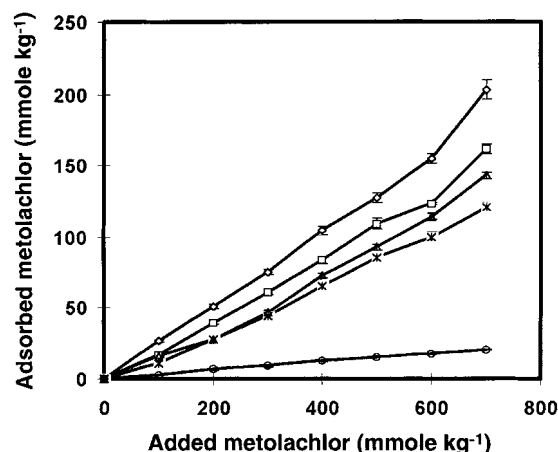
Detailed information on the adsorption isotherms of these organic cations has been reported previously.<sup>39</sup> The organo-clay complexes prepared and used in this study were clay preadsorbed with BTMA and BTEA at loads of 0.5 or 0.8 mole kg<sup>-1</sup> clay.

### 3.2 Adsorption isotherms

The adsorption isotherms of metolachlor on clay (Mont) and clay pre-adsorbed with either BTMA or BTEA at loads of 0.5 or 0.8 mole kg<sup>-1</sup> clay at 25 °C are shown in Fig 2. Metolachlor was added up to its solubility limit in water (530 mg litre<sup>-1</sup>). As expected, the herbicide was poorly adsorbed on montmorillonite alone, whereas adsorption of metolachlor on clay pre-adsorbed with BTMA was increased more than 10-fold. Intermediate enhancement of metolachlor adsorption resulted by clay-BTEA

### 3.3 FTIR

Infrared spectroscopy provided detailed information

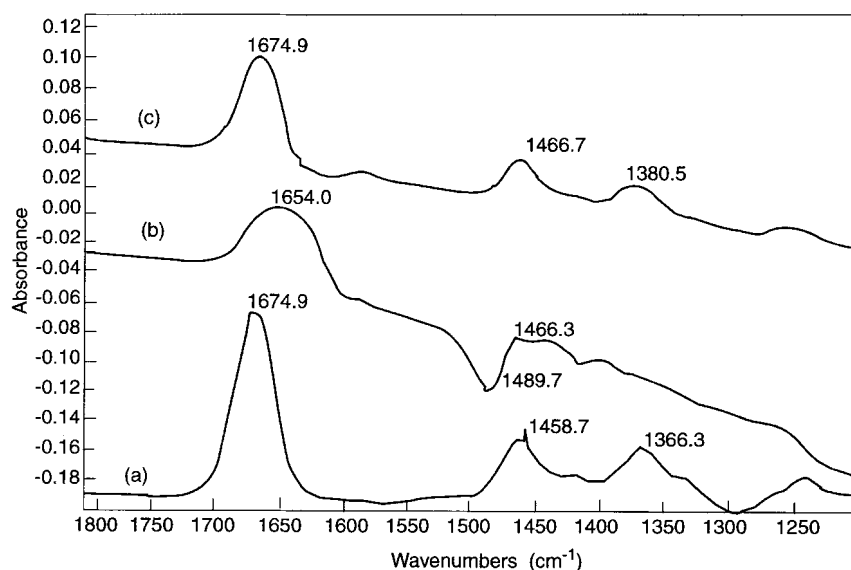


**Figure 2.** Adsorption isotherms of metolachlor on (●) montmorillonite alone, montmorillonite pre-adsorbed with BTMA (◇) 0.5 or (□) 0.8 mole kg<sup>-1</sup>, and BTEA (\*) 0.5 or (△) 0.8 mole kg<sup>-1</sup> clay. Bars indicate standard errors.

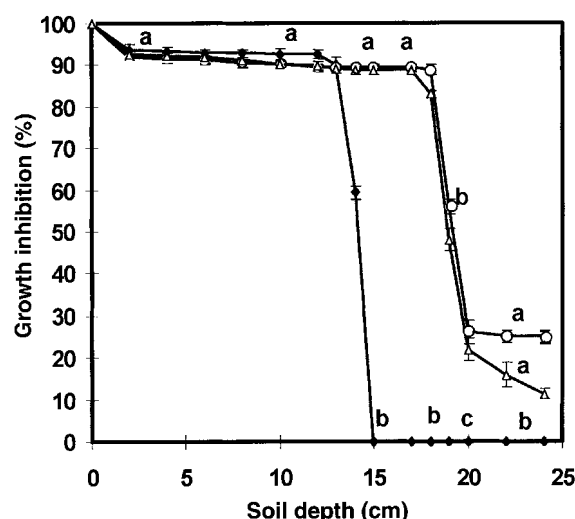
on the intermolecular interactions between metolachlor molecules and the organo-clay complex. Figure 3 shows the difference spectra of metolachlor (a) in its free form (b), adsorbed to clay pre-adsorbed with BTMA and (c) with BTEA at a load of 0.8 mole kg<sup>-1</sup> clay. The three peaks in the spectrum of free metolachlor were assigned to the stretching vibrations of C=O group (1674.9 cm<sup>-1</sup>), phenyl ring (1458.7 cm<sup>-1</sup>) and the anilidic group C-N, (1366.3 cm<sup>-1</sup>).<sup>40</sup> The main differences among the three spectra are shifts of the peak 1674.9 cm<sup>-1</sup> to a lower wave number of 1654 cm<sup>-1</sup> (b) and not shifted (c). The peak at 1458.7 cm<sup>-1</sup>, the stretching vibration of the phenyl ring (a) shifted to 1466.3 cm<sup>-1</sup> with an inverted peak at 1489.7 cm<sup>-1</sup> (b) and to 1466.7 cm<sup>-1</sup> (c). The peak at 1366.3 cm<sup>-1</sup>, of the free metolachlor (a) disappeared in (b) and shifted to 1380.5 cm<sup>-1</sup> in (c).

### 3.4 Leaching studies

Results of laboratory experiments using soil columns



**Figure 3.** Fourier-transform infrared (FTIR) absorption spectra of (a) free metolachlor and metolachlor adsorbed to montmorillonite pre-adsorbed by (b) BTMA at a load of 0.8 mole kg<sup>-1</sup> and (c) BTEA at a load of 0.8 mole kg<sup>-1</sup> clay.

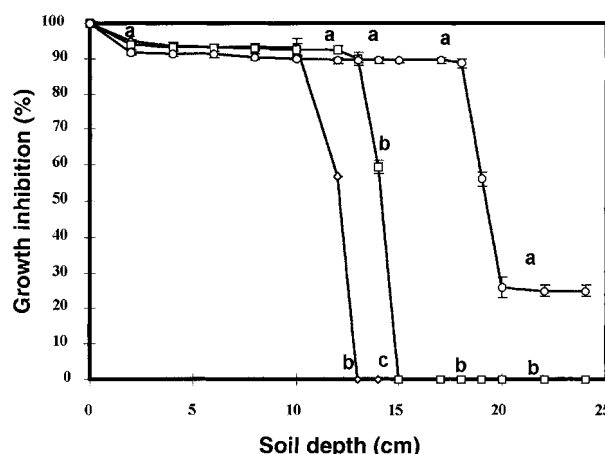


**Figure 4.** Leaching of different formulations of metolachlor ( $2.0 \text{ kg ha}^{-1}$ ) in columns filled with sandy soil following irrigation with  $500 \text{ m}^3 \text{ ha}^{-1}$ . Green foxtail growth was used to estimate the presence of metolachlor. Metolachlor formulations were (○) commercial EC; (△) metolachlor on clay alone; (♦) metolachlor on clay pre-adsorbed with BTMA  $0.5 \text{ mole kg}^{-1}$  clay. The clay-based formulations contained 13% metolachlor and were prepared by adding the herbicide in acetone solution. Means followed by the same letter at a representative depth are not significantly different at  $P=0.05$  level. Bars indicate standard errors.

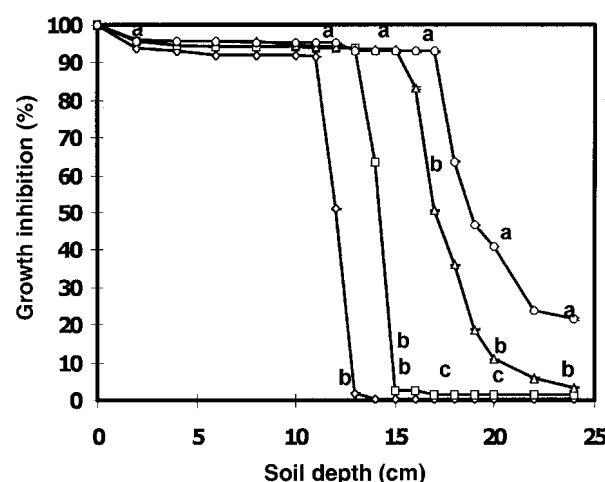
have shown that the commercial metolachlor EC applied pre-emergence at the recommended rate ( $2.0 \text{ kg AI ha}^{-1}$ ) followed by irrigation at  $500 \text{ m}^3 \text{ ha}^{-1}$  leached to a layer of 0–18 cm (Fig 4). The reduction in plant height of the test plant and the percentage growth inhibition at this layer was about 95%. The herbicidal activity detected below that depth declined rapidly. Similar mobility of metolachlor in soil has been reported previously.<sup>41</sup> Formulating metolachlor with montmorillonite without any pre-adsorption with organic cation did not bring about any reduction of leaching compared to that of the commercial formulation. Formulating metolachlor (dissolved in acetone) with clay pre-adsorbed with BTMA at a load of  $0.5 \text{ mole kg}^{-1}$  resulted in a significant inhibition of leaching, and with herbicidal activity limited to the top 14 cm (Fig 4).

A formulation prepared by adding metolachlor in aqueous solution to clay pre-adsorbed with BTMA at a load of  $0.5 \text{ mole kg}^{-1}$  clay was more effective in reducing the leaching of metolachlor. Its herbicidal activity was limited to the top 11 cm as compared to the commercial EC formulation or to the organo-clay formulation prepared by adding metolachlor in organic solvent that leached to a depth of 14 cm. (Fig 5).

Adding metolachlor (dissolved in acetone) at a lower load of  $50 \text{ g kg}^{-1}$  to clay pre-adsorbed with BTEA at a load of  $0.8 \text{ mole kg}^{-1}$  clay resulted in a significant reduction in the leaching, with herbicidal activity limited to the top 11 cm of the soil depth as compared with the higher loads (Fig 6). Clearly, a lower load of metolachlor enhances the chances for a



**Figure 5.** Leaching of different formulations of metolachlor ( $2.0 \text{ kg ha}^{-1}$ ) in columns filled with sandy soil following irrigation with  $500 \text{ m}^3 \text{ ha}^{-1}$ . Green foxtail growth was used to estimate the presence of metolachlor. Metolachlor formulations were (○) commercial EC; (♦) metolachlor on clay pre-adsorbed by BTMA  $0.5 \text{ mole kg}^{-1}$  clay, prepared by adding the organo-clay complex to metolachlor dissolved in water and (□) by adding the organo-clay complex to metolachlor dissolved in acetone. Means followed by the same letter at a representative depth are not significantly different at  $P=0.05$  level. Bars indicate standard errors.



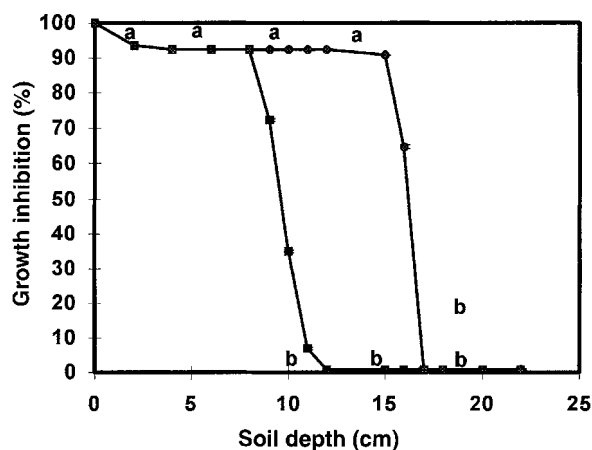
**Figure 6.** Leaching of different formulations of metolachlor ( $2.0 \text{ kg ha}^{-1}$ ) in columns filled with sandy soil following irrigation with  $500 \text{ m}^3 \text{ ha}^{-1}$ . Green foxtail growth was used to estimate the presence of metolachlor. Metolachlor formulations were (○) commercial EC and metolachlor at loads of (♦) 50, (□) 130 or (△)  $300 \text{ g kg}^{-1}$  on clay pre-adsorbed by BTEA  $0.8 \text{ mole kg}^{-1}$ . Means followed by the same letter at a representative depth are not significantly different at  $P=0.05$  level. Bars indicate standard errors.

direct interaction of its molecules with the organo-clay surface.

Under field conditions (Fig 7) the Mont-BTMA  $0.5 (\text{mole kg}^{-1})$  formulation was active in the top 0–10 cm of the soil profile, whereas the commercial formulation was active in the top 0–16 cm. These results are in agreement with the results of the laboratory experiments indicating that the organo-clay based formulation leaches less than the commercial formulation.

### 3.5 Phytotoxicity

The response of green foxtail to different levels of



**Figure 7.** Leaching of (●) commercial EC of metolachlor and (■) Mont-BTMA 0.5 mole kg<sup>-1</sup> clay containing 130 g kg<sup>-1</sup> metolachlor under field conditions using green foxtail as a test plant. Metolachlor was applied at 2.0 kg ha<sup>-1</sup> followed by irrigation of 500 m<sup>3</sup> ha<sup>-1</sup>. Means followed by the same letter at a representative depth are not significantly different at  $P=0.05$  level. Bars indicate standard errors.

several formulations of metolachlor applied pre-emergence in pots under greenhouse conditions is similar. All formulations of metolachlor caused similar growth inhibition. The growth of test plants in pots treated with organo-clay alone without the active ingredient of the herbicide was similar to the growth in the control samples. This indicates that the organo-clay complexes alone had no toxic effects to the test plants.<sup>42</sup>

#### 4 DISCUSSION

The quaternary ammonium cations used for preparing the organo-clay based formulations are classified as surface-active agents (surfactants), because each molecule has a non-polar hydrocarbon group and an ionic, polar component. All of the selected quaternary ammonium compounds have an aromatic functional group similar to that of metolachlor. The low adsorption of metolachlor to the unmodified clay is due to the hydrated surface of the clay, and the hydrophobicity of metolachlor molecules. The adsorption of metolachlor to the complex increases almost linearly as its concentration in the equilibrium solution is increased. The dramatic increase in the adsorbed amounts of metolachlor to the clay pre-adsorbed with BTMA at a load of 0.5 mole kg<sup>-1</sup> is likely due to the interaction of metolachlor molecules with the clay surface whose hydrophilic nature has been modified by the adsorbed organic cation. The efficiency of adsorption of metolachlor followed the sequence Mont-BTMA 0.5 > Mont-BTMA 0.8 > Mont-BTEA 0.8 > Mont-BTEA 0.5 >> Mont, namely metolachlor adsorption by Mont-BTEA is weaker relative to the uptake by Mont-BTMA, but it is still significantly higher than the uptake by the clay alone. A possible explanation for that may be the size and the shape of the organic cation molecules as previously

**Table 1.** Binding constant of metolachlor adsorbed to organo-clay surfaces

System	$K$ (M <sup>-1</sup> )	$R^2$	RMSE <sup>a</sup> (mmole kg) <sup>-1</sup>
Clay alone	45	0.99	0.7
Clay-BTMA 0.5 mole kg <sup>-1</sup>	680	0.96	11
Clay-BTMA 0.8 mole kg <sup>-1</sup>	480	0.97	8.9
Clay-BTEA 0.5 mole kg <sup>-1</sup>	340	0.97	6.3
Clay-BTEA 0.8 mole kg <sup>-1</sup>	400	0.95	10

<sup>a</sup> Root mean square error.

reported for alachlor,<sup>33</sup> and for other cases.<sup>43</sup> Increasing the length of side chain (-CH<sub>3</sub>) in the cation BTMA to (-C<sub>2</sub>H<sub>5</sub>) in the cation BTEA, resulted in a decrease of the adsorbed amounts of metolachlor, perhaps due to steric hindrance.

Under the same conditions, the amount of alachlor adsorbed was greater than that of metolachlor. The lower affinity of metolachlor to be bound with an organo-clay complex is correlated with the relative higher solubility in water of metolachlor which has a lower log  $P$  (2.9) than that of alachlor (3.09). It has been reported that compounds with lower water solubility are adsorbed to a greater extent on soil organic matter than are compounds of higher solubilities.<sup>44</sup>

In Table 1 we present a summary of fitting the results in Fig 2 to Scatchard plots following the procedure in Nir *et al.*<sup>45</sup> The definition of the root mean square error, RMSE, is given by the following equation:

$$\text{RMSE} = \left[ \sum_{i=1}^n (Y_{i,e} - Y_{i,c})^2 / (n - 1) \right]^{1/2} \quad (2)$$

in which  $n$  is the number of data points (7), and  $Y_{i,e}$  and  $Y_{i,c}$  are the experimental and the calculated adsorbed amounts in units of mole kg<sup>-1</sup>. The results in Table 1 indicate good fits of the measured curves to Scatchard plots with  $R^2$  values close to unity and the values of the deviations between experimental and calculated adsorbed amounts being within the experimental uncertainty. A partition model could not explain the results of metolachlor adsorption to the organo-clays. It is of interest that for adsorption to the clay alone the  $k$ -value of the less soluble herbicide, alachlor, (50 M<sup>-1</sup>) (data not shown) which is presumably more hydrophobic than metolachlor, is just 10% higher than that of metolachlor. However, the  $k$ -value for the adsorption of alachlor to the modified clay, eg BTMA 0.5 (1000 M<sup>-1</sup>) (data not shown) is 32% higher than that of metolachlor (Table 1).

It can be seen from the FTIR spectra in Fig 3 that the interactions between metolachlor molecules and the organo-clay surface are stronger in the case of BTMA. It can be observed that the molecular structure of the quaternary ammonium cation affects both the magnitude of adsorption of metolachlor (Fig 2) and the mode of its interactions with the organo-

clay surface (Fig 3). The results suggest the existence of interaction between the phenyl ring of the aromatic cations (BTMA and BTEA) and the phenyl ring of metolachlor molecules, possibly by  $\pi - \pi$  interactions, and hydrogen bonding via the carbonyl and the anilidic groups, in accord with similar results with alachlor and suggestions for other cases.<sup>46</sup>

The significant reduction in leaching of metolachlor when formulated with clay-BTMA at a load of 0.5 (Fig 4) is due to the interaction between metolachlor molecules and the hydrophobic sites generated on the clay surface as a result of pre-adsorption with organic cation.

A possible explanation for the leaching result presented in Fig 5 is that when using an organic solvent for preparing the organo-clay formulation, part of the added metolachlor is loosely bound. Less leaching was observed by employing the complex Mont-BTMA 0.5 than Mont-BTMA 0.8 mole kg<sup>-1</sup> clay, as was also observed with alachlor.<sup>33</sup> Thus, reduced leaching of the herbicide correlates with its enhanced adsorption to the organo-clay complex.

A possible explanation for the leaching result presented in Fig 6 is that, at the lower rate of metolachlor, the ratio of organo-clay/metolachlor is higher, increasing the possibility for each molecule to interact directly with BTMA molecules on the clay surface.

It is evident from the data in Fig 7 that the organo-clay based formulation leaches less than the commercial EC formulation. This behaviour of the organo-clay formulation under field conditions is due to two reasons. First, under field conditions, metolachlor may move in two directions, horizontal and perpendicular. Second, in addition to the downward movement in water rainfall or irrigation there is an upward movement of herbicide in response to water evaporation. The adsorption of metolachlor to the organo-clay also reduces its possible loss by volatilization or photodegradation.<sup>42</sup>

Since water evaporation is more pronounced under field conditions, it reduces the downward movement. This retention reduces the hazards of contamination of ground water.

Our results demonstrate the advantage in the application of a clay-BTMA formulation of metolachlor, which gave high herbicidal activity in the top soil and minimal leaching. It can be seen that the use of a smaller organic cation BTMA in the formulation maintained the threshold concentration needed for weed control in the top soil. It also provides a longer period of weed control due to the slow release of the active ingredient to the soil environment and a protection of ground water from contamination.

## 5 CONCLUSIONS

1. In designing clay-based formulations of metolachlor with reduced leaching it is advantageous to pre-adsorb an organic cation whose structure would enable

optimal interactions between the molecules of the herbicides and the surface sites of the organo-clay complexes, rather than merely modify the clay surface from hydrophilic to hydrophobic.

2. The degree of coverage of the clay surface by the organic cation has to be optimized. Loading the clay to its CEC with the organic cation does not necessarily imply optimal interactions between the herbicide and the organo-clay complex. A similar conclusion was reached in our studies on alachlor.

3. Organo-clay formulations of metolachlor prepared by addition of an aqueous solution of the herbicide were better in reducing leaching than those employing acetone solutions. The application of the new organo-clay formulations of metolachlor may retain the active ingredient in the top soil layer, which makes it available for biodegradation and thus reduces the hazard of ground water contamination.

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